

SELF-SENSITIZATION OF PHOTO-CHLORINE EVOLUTION IN AQUEOUS DISPERSIONS OF SILVER ZEOLITES

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Summary

Self-sensitization means that systems which are first insensitive to light of a certain wavelength become photoactive after they have been illuminated with light of higher energy. We have succeeded in measuring self-sensitization of photo-chlorine evolution in aqueous dispersions of silver zeolites containing Cl^- ions. To carry out these measurements we have developed a very sensitive Clark-like chlorine detector which can be used in the liquid phase as well as in the gas phase.

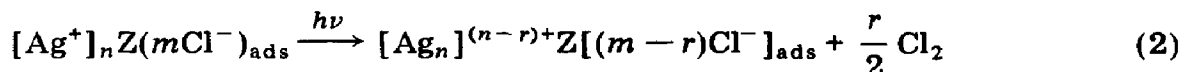
1. Introduction

It has been mentioned several times in the literature that the reaction



could potentially be very useful for photochemical solar energy conversion [1 - 3]. Anodic photocurrents were observed at silver electrodes when the electrolyte contained halide ions. For hole formation it was speculated that reaction (1) takes place [4]. We have observed that below pH 4 aqueous silver zeolite dispersions produce Cl_2 in the presence of Cl^- when irradiated at 360 nm [5]. On changing from acid to neutral or alkaline conditions a change from chlorine to oxygen production was observed. The question remained how this reaction could be sensitized; organic dyes used in the photographic process [6] are not stable enough. Recently we have detected self-sensitization of photo-oxygen evolution in an aqueous dispersion of silver zeolite A. Self-sensitization means that a system which is first insensitive to light of a certain wavelength becomes photoactive after it has been illuminated with light of higher energy. In a computer-controlled experiment, which allowed us to keep parameters constant and to collect data for several days, we proved that self-sensitization really occurred [7]. Later

we found that the photo-chlorine evolution of an aqueous silver zeolite dispersion



shows a similar type of self-sensitization [8]. To obtain precise experimental information it was necessary to develop a sensitive chlorine detector.

2. Chlorine detection

Clark sensors, which can be bought from several manufacturers, are widely used for oxygen detection under different conditions. They have been described in detail in the literature [9]. We and others have shown how Clark sensors can be used for hydrogen detection in the gas phase as well as in the liquid phase [10 - 12]. Since this type of sensor is very convenient in photochemical experiments we have used the same principle for the Cl_2 detection in our measurements. As far as we know, nobody has used Clark-like sensors for chlorine detection up to now. We therefore describe the necessary details for this measurement technique to be successfully used. Because of the many chlorine compounds found in aqueous solutions depending on the pH [13], an appropriate membrane is needed. We use a commercial Clark oxygen sensor from WTW, West Germany. As a membrane we use Fluoropor R type FH 0.5 μm from Millipore. The potential of the working electrode is held at -200 mV *versus* $\text{Ag}/\text{Ag}_2\text{SO}_4$. At this potential the sensor is insensitive towards oxygen but very sensitive towards Cl_2 . To calibrate the sensor we apply a procedure similar to that described for oxygen detection [7]. A hypochloric acid solution is injected into 100 ml of an acidic aqueous solution (pH 2 and 0.2 M KCl). The chlorine is formed according to the reaction



As in the case of H_2 or O_2 , the response of the sensor is faster if it is immersed in the solution and the sensitivity is therefore much higher. The nitrogen flow through the reactor (total volume, about 150 ml) was kept constant at 50 ml min^{-1} by means of a double-needle valve. The temperature was held constant at 20 °C. The result of such a calibration is shown in Fig. 1 which proves that the sensitivity of this detector is very high. In photochemical experiments one has to be aware that light can cause unwanted signals, so the sensor should be shielded.

3. Self-sensitization experiment

It is interesting that reaction (2) is observed despite the large driving force for the back reaction ($\text{Ag}, \text{AgCl}|\text{HCl}(1 \text{ M})|\text{Cl}^-, 1/2\text{Cl}_2, E^0 = 1.14 \text{ V}$). A phenomenological understanding of this behaviour can be derived from the observation that a silver rod, covered with AgCl and immersed in an acidic

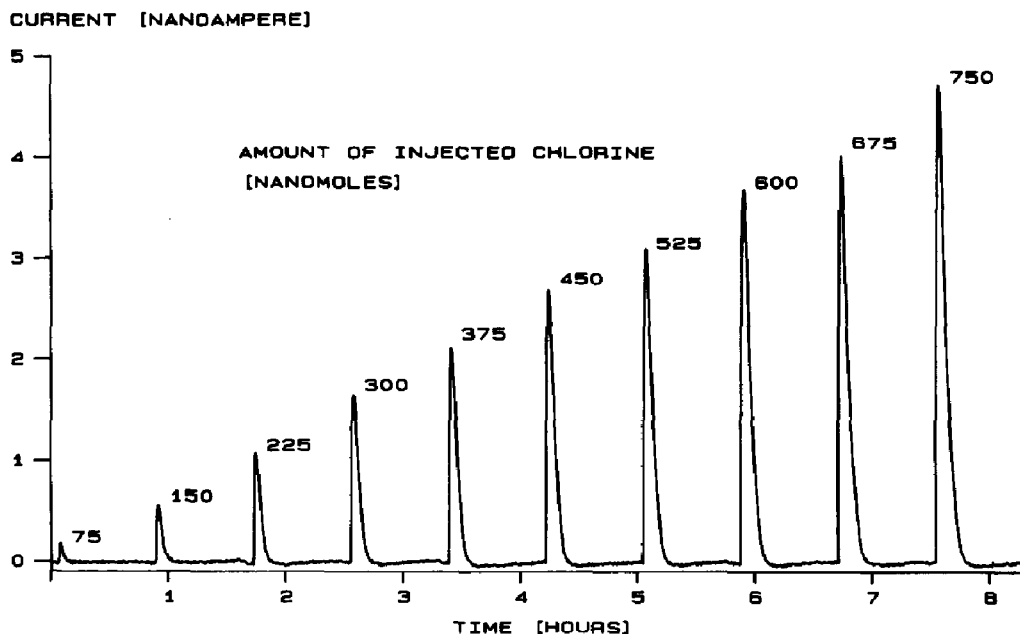
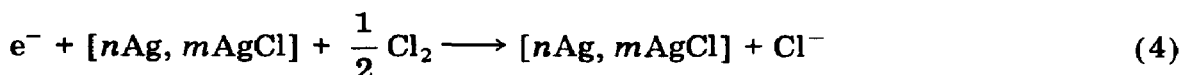
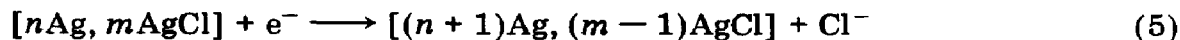


Fig. 1. Calibration signals of the Clark chlorine detector. (The numerals on each peak indicate the number of nanomoles of Cl_2 .)

HCl solution, remains at the Ag/AgCl potential if Cl_2 is added. This means that the electrode reaction



is very slow, whereas we know from the high reversibility of Ag/AgCl electrodes that the reaction



is very fast.

To prove that self-sensitization occurs in reaction (2) we have carried out experiments similar to those for photo-oxygen evolution. The same experimental set-up was used and for the details we refer the reader to our previous paper [7]. To make sure that no stray light affected the observations, cut-off filters were employed: 389 nm for the 410 nm irradiation, 435 nm for the 450 nm irradiation and 475 nm for the 490 nm irradiation. The light flux in the experiment (Fig. 2) was 9 mW and the total illuminated area was 25 cm^2 . In this experiment 400 mg of silver zeolite $\text{Ag}_{7.7}\text{Na}_{2.3}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 24\text{H}_2\text{O}$ was dispersed in 100 ml of an 0.2 M KCl solution. A pH of 3.8 was obtained by adding hydrochloric acid. In contrast to photo-oxygen evolution the pH remained constant during the whole reaction. This is as expected from the stoichiometric equation, but the behaviour of chlorine in aqueous solutions is complicated [13].

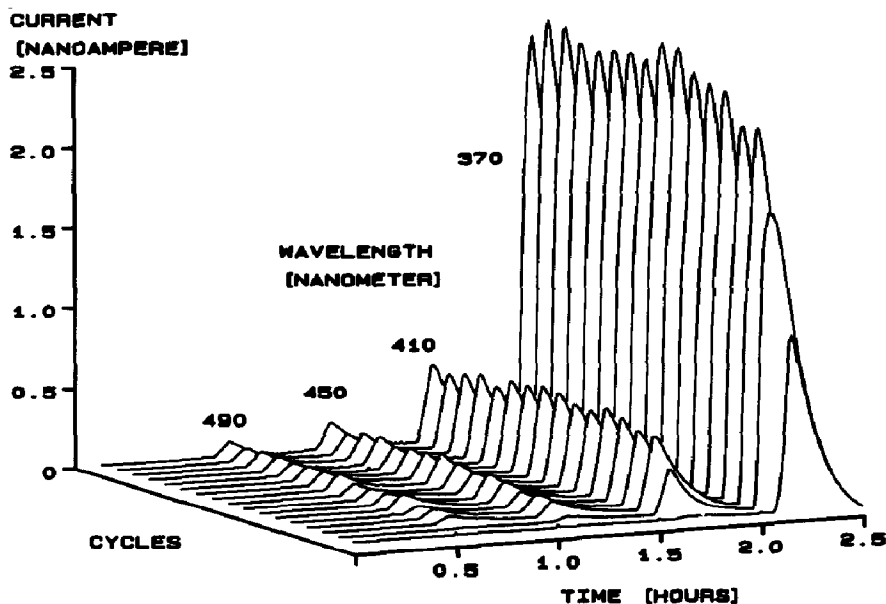


Fig. 2. Self-sensitization experiment of an aqueous zeolite A dispersion in the presence of Cl^- . (1 nanoampere corresponds to 208 nanomoles of Cl_2 .)

17 cycles are shown in Fig. 2, each starting at 490 nm. At each wavelength indicated, the dispersion was irradiated for 5 min. The slit width of the monochromator corresponded to 30 nm. After the 370 nm irradiation, a dark period of 30 min was included to allow the Cl_2 to disappear completely. Since Cl_2 can only be removed slowly by a stream of nitrogen a graphite rod was immersed in the dispersion after each irradiation. It is known that zeolite A hydrolyses at acidic pH [14]. This does not affect the important result of our experiment which proves that self-sensitization of photochlorine evolution occurs in aqueous dispersions of silver zeolites. For practical applications it might be desirable to substitute zeolite A by a zeolite which is more stable under slightly acidic conditions. We have found that Mordenit which is stable against hydrolysis works as well as zeolite A.

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